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AN EXPERIMENTAL STUDY OF THE SITE AND MODE OF ACTION OF PLATONI--ETC(U)
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**AIAA Paper
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AN EXPERIMENTAL STUDY OF THE SITE AND MODE
OF ACTION OF PLATONIZERS IN DOUBLE BASE PROPELLANTS

by
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**AIAA 12th Aerospace
Sciences Meeting**

WASHINGTON, D.C. / JANUARY 30-FEBRUARY 1, 1974

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AN EXPERIMENTAL STUDY OF THE SITE AND MODE OF ACTION
OF PLATONIZERS IN DOUBLE BASE PROPELLANTS

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Abstract

Certain metal organic salts (e.g., lead or copper salicylate) when used in double base propellants induce desirable insensitivities of burning rate to pressure and initial temperature. To understand this, the combustion wave zones (luminous flame, dark, fizz, and surface reaction zones) were examined by means of photography and fine thermocouples (4 micron bead). The metal salts significantly alter the surface and fizz zones. The surface zone accumulates carbonaceous material coincident with the appearance of an accelerated burning rate in the catalyzed case. No attendant change in surface heat release is detected. Coinciding with this carbonaceous layer occurrence are substantial (50 to 100%) increases in conductive feedback from the fizz zone. This latter effect is believed directly responsible for the altered burning behavior though its origin may lie in the altered surface chemistry.

Introduction

The ballistic properties of nitrate ester propellants can be greatly improved by minor additions (1 or 2 percent) of certain heavy metal organic salts (such salts are commonly referred to as catalysts though they may not meet the classical definition of this term). The properties most affected are burning rate sensitivity to pressure and initial temperature. These properties can be made desirably small (or even slightly negative) in the rocket pressure regime by means of such additives.

The heavy metal salts of greatest practical usefulness are those of lead. Copper salts are frequently added also, the combination of the two providing a synergistic enhancement of ballistic properties. A wide variety of organic moieties has been employed to shift the region of improved properties to various design pressure levels. Lead and copper salicylate are representative additives that are effective in the neighborhood of 70 atm.

The detailed effect of such additives on burning behavior can be seen more clearly on a plot of burning rate vs pressure (see Fig. 1). A typical double base, nitrate ester propellant with no catalytic additive exhibits a fairly constant pressure exponent (slope on the log-log plot); its value is typically between 0.7 and 0.8, implying decreased rocket motor stability. As Fig. 1 indicates, catalyst addition produces a characteristic alteration of the burning rate-pressure relation. Over a large fraction of the pressure range, the burning rate is considerably increased (as much as a factor of three); this boost in burning rate is termed the super rate. This super rate disappears with increased pressure resulting in a region of near-zero pressure exponent (a plateau, hence, the term platonizer for the catalyst) and, in some cases, a negative exponent (a mesa). Beyond this region, the burning rate approaches that of the noncatalyzed propellant. As indicated above, the plateau (and mesa) region, with its low pressure exponent and insensitivity to ambient temperature (not shown in the Figure) provides an ideal operating regime for stable motor operation. This research concerns the mechanism that underlies this catalyst induced change in burning behavior.

The catalyst clearly must produce substantial alterations in the details of the propellant burning mechanism. However, the gross, visible features of the combustion wave are not greatly changed; the general structure of the wave (temperature vs distance) is shown in Fig. 2. The successive zones are referred to as the subsurface (or surface), fizz, dark and visible flame zones. While the catalyst does not visibly produce violent distortions of these zones, it could conceivably produce its effects on burning behavior by altering the kinetics and/or energetics in one or all of them.

A variety of explanations of the role of the catalyst have been offered. (1,2,3,4,5) Two of these are most prominent, that of Camp et al (2) and that of Powling, et al. (4) Camp proposed that the super rate

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Performed in the Aerospace and Mechanical Sciences Department of Princeton University under contract N00014-67-A-0151-0023 issued by the Power Branch of the Office of Naval Research.

Index Category: Properties of Fuel & Prop., Comb. in Heterogeneous Media.

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burning is a consequence of a photochemical enhancement of the degradation reactions in the surface (and subsurface) zone. The source of the radiation is the luminous flame zone; this radiation is purportedly strengthened by lead and copper (when present) line radiation due to the presence of the metal vapors in the flame. Disappearance of the super rate (which produces a plateau or mesa) is a consequence of physical blockage of the radiation before it reaches the condensed phase by some mechanism such as lead metal accumulation on the burning surface.

Powling, et al, unlike Camp, proposed that the basic burning mechanism of the nitrate esters is not fundamentally altered but rather is accelerated by catalysis. Some fraction of the degrading nitrate esters normally forms a carbonaceous char on the burning surface. Addition of a lead salt yields a complex metal-carbon catalyst which can accelerate the reduction of NO above the burning surface; this accelerates the energy feedback to the surface and induces the super rate burning. At high pressures, however, the NO purportedly oxidizes the carbon as fast as it forms thus precluding the catalytic acceleration; the super rate disappears producing the plateau or mesa.

Neither of these proposed models is fully consistent with all known experimental facts. Thus, at the outset of the present work there was not full knowledge of how the zones of the combustion wave are affected by the catalytic additives nor by what mechanism these effects yield the appearance and disappearance of super rate burning. The present study was undertaken to help clarify this issue. The tools used here are largely photographic observation and very fine thermocouples.

The experimental investigations were carried out with particulate nitrocellulose (PNC, 12.6%N) and trimethylolethane trinitrate (TMETN) double base propellants rather than the more hazardous to formulate nitrocellulose (NC) and nitroglycerin (NG) propellants; the compositions of the propellants used in this study are shown in Table I. The present system is similar to that reported by Camp;⁽⁶⁾ it is a useful system of moderate energy and good flexibility.⁽⁷⁾ The qualitative appearance of the combustion waves for both systems is quite similar. Inspection of Fig. 3, shows that with similar catalytic additives and total energies the two propellant systems also exhibit quite similar burning rate curves. Thus, it is reasonable to expect that results and conclusions for the PNC/TMETN propellants carry over to those made from NC/NG.

Referring again to Fig. 2, one sees that there are four defined zones where the catalyst might conceivably exert its

effects. Consider first the luminous flame zone. A substantial fraction of the propellant energy is released here. If an appreciable amount of this energy release is conducted back toward the propellant surface, it could strongly influence the burning rate. Measurements of the stand-off distance of this luminous flame from the propellant surface (called dark-zone length) have been made previously for a variety of propellants;^(8,9,10) they have been repeated here for the PNC/TMETN system (see Fig. 4). The results immediately cast doubt on the importance of feedback from the luminous flame zone since the measured distances imply extremely small feedback fluxes (e.g., from Fig. 4, the 1 cm stand-off distance at 20 atm for propellant 1031 implies a feedback flux less than 1 cal/cm²sec). Furthermore, the results in Fig. 4 show a trend opposite to that expected if conductive feedback from the luminous flame controlled burning rate - instead of the expected decrease in stand-off distance with increased burning rate; an increase of this distance is seen. Finally, similar measurements for standard NC/NG propellant N-5, whose burning rate behavior is shown in Fig. 3, show that the stand-off distance decreases monotonically throughout the high pressure range even though the burning rate first increases then decreases (forming a mesa). None of these facts is consistent with the notion that the super rate results from catalyst effects on conductive feedback from the luminous flame. While the catalyst does have some effect on the energetics of the luminous flame⁽³⁾, this is not the cause of super rate burning and platonization.

These results concerning stand-off distance do not preclude the role for the luminous flame hypothesized by Camp,⁽²⁾ i.e., a source of radiation for rate-accelerating photochemical reactions in the condensed phase. However, it should be noted that for the present propellant system, the luminous flame disappears below about 7 atm. The super rate, however, persists to lower pressures, being about 30% of the base rate at 1 atm; this is not consistent with the Camp model.*

The measurements shown in Fig. 4 can also provide information on the influence of the catalyst on the dark zone. Starting from the energy equation for the dark zone, ignoring the demonstrably small conduction terms and linearizing the temperature gradient, one can show⁽¹¹⁾ that dark zone length has the following pressure dependence:

$$L_{dz} \sim p^{m-n} \sim p^d \quad (1)$$

*We have had private communications with Camp on this matter. He now believes that a photochemical mechanism may be operative only with certain metal organic salts that produce plateaus at much higher pressures than those studied here; the results of this study are not in conflict with this hypothesis.

Here L_{dz} is the measured dark zone length, p is the pressure, m is the burning rate exponent (slope on a plot such as Fig. 1), d is the dark zone pressure exponent (slope on L_d plot in Fig. 4) and n is the effective overall order for reactions in the dark zone. From Fig. 4, one sees that m and d are fairly constant over a broad pressure range for both the catalyzed and noncatalyzed formulations. Thus the effective reaction order in the dark zone can be computed; this same computation can be done for other published data. (8,10,12) Table II summarizes the results. It appears that all of these formulations, whether catalyzed or not, have an effective reaction order in the dark zone of about 2.5. This suggests common chemical pathways unchanged by catalyst addition.

Another means of gauging the catalyst influence on the dark zone is by its effect on the overall reaction time there. The fractional decrease in time, termed here the catalyst activity, is given by

$$\eta_d \equiv 1 - (\tau_{cat}/\tau_{uncat}) = 1 - \left(\frac{r_{uncat} L_{dz,cat}}{r_{cat} L_{dz,uncat}} \right) \quad (2)$$

where, by definition, $\tau = L_{dz}/V_{gas}$ and the gas velocity V_{gas} is eliminated via the mass continuity relation across the propellant/gas interface; this brings in the burning rate r . The only approximation above is that the two types of propellants have nearly equal dark zone temperatures; this is found to be so experimentally (see Fig. 7).

When this catalyst activity is computed for various pressures from the results in Fig. 4, the result yields Fig. 5a; Fig. 5b is a similar result for other propellant compositions. In Fig. 5a, the fractional decrease in dark zone reaction time is only about 0.3 for pressures greater than 20 atm; it increases to about 0.6 in the low pressure region where the relative burning rate increase due to catalysis is also a maximum. This similarity in trends is not seen for the propellants shown in Fig. 5b. The values of η_d are comparable or less than in Fig. 5a and the super rate effects substantially less. These figures show that the dark zone reactions are somewhat accelerated but it is not clear from this whether this degree of acceleration can substantially increase the burning rate.

Crawford⁽⁹⁾ found that metallic nickel shortened L_{dz} by an order of magnitude with essentially no effect on burning rate. η_d computed from this result is approximately 0.9. This indicates that the substantially smaller values in our experiments are unlikely to account for a significant portion of the super rate.

The same photographs that provided the dark zone data in Fig. 4 show some poorly defined but persistent differences between the catalyzed and noncatalyzed propellant

flames. The use of infrared film (Kodak High Speed Infrared) brings out these differences much more sharply. Figure 6 shows a series of such photographs at a single pressure with various additive combinations. One sees that catalyst presence is accompanied by a large amount of particulate emission from the burning surface; these particles persist over large distances in the flame. The particle size depends strongly on whether the catalyst contains lead or copper (and so does the burning rate) implying some substantial differences in the action of these two types of metallic salts. The combination of the two catalysts yields a high emission rate of small particles and the highest burning rate. High speed motion pictures of the burning surface with external illumination reveal that the particles are largely carbonaceous-appearing, filamentous structures formed in an irregular sequence on the burning surface; a similar process for NC/NG propellants was described in Ref. 4. Some small fraction of the particles may also be direct degradation products of the catalyst, e.g., metallic lead particles have been found to be ejected from the surface by previous investigators. (13)

From Fig. 6, one can conclude that some substantial alteration in the surface and subsurface zone chemistry must occur in order to increase the formation of carbonaceous material. Whether this effect in some way yields an accelerated burning rate requires further investigation.

Very fine thermocouples provide considerable information about the energetics of the combustion wave and, in particular, the region near the surface. The thermocouples used here were made from 2.5 micron diameter platinum and platinum/10% rhodium Wollaston wire; only thermocouples with a junction size of 4 microns or less were selected for use. Manufacture and imbedding of such delicate thermocouples requires special care; procedures are described in Ref. 11. Even this very small junction size begins to become comparable to the thickness of the surface region reaction zones (subsurface and fizz zones) at pressures of approximately 25 atm and above. Thermocouple traverses were therefore made only up to 21 atm; even at this pressure the actual temperature gradients may be somewhat higher than the recorded values.

A typical set of thermocouple results is shown in Fig. 7; for convenience, the curves were drawn through common points at 350°C (except for $p < 1$ atm). An important difference between the two types of propellants is evident. The catalyzed propellants exhibit a greater temperature gradient just above the surface, i.e., in the fizz zone. This indicates that the conductive heat feedback from the fizz zone is consistently higher for catalyzed propellants. Note also that the final temperature at the end of the fizz zone for the catalyzed case is the same or less than that for the noncatalyzed case. This is inconsistent with Powling's model which hypothesizes a greater total heat release in this zone.

Figure 8 shows this result more clearly; here the slope in the gas at the surface, from plots such as those in Fig. 7, is plotted vs pressure and catalyst presence. The scatter is somewhat high as is usual in this type of measurement but the trend is clear. At the high pressure side of the graph, where Fig. 5 indicates the base burning rate is more than tripled by catalysis, the conductive feedback flux from the fizz zone has been doubled. Referring again to Fig. 7, one sees that the increased feedback is not the result of a substantial increase in final fizz zone temperature. Thus the increase is a consequence of accelerated reaction chemistry rather than an increase in fizz zone heat release.

Further information can be extracted from the thermocouple traverses of Fig. 7. Experimentally one finds that the emergence of the thermocouple through the burning surface and, therefore, the surface temperature are signalled by a fairly abrupt increase in random fluctuations superimposed on the thermocouple output (see Ref. 11 for details). The values obtained in this manner are shown in Fig. 9; they are generally consistent with, though somewhat lower than, the values obtained by previous investigators for NC/NG systems. (14,15,16) As expected, the catalyzed propellant has a slightly higher surface temperature reflecting its higher burning rate; in addition, the temperatures for both propellants increase weakly with increasing pressure as, again, the burning rate increases.

Finally, one can combine the information from Fig. 8 and Fig. 9 with a surface energy balance to obtain an estimate of the surface energy release.

$$\lambda_g \left(\frac{dT}{dx} \right)_{s,g} + r \rho_p Q_s = \lambda_s \left(\frac{dT}{dx} \right)_{s,p} = r \rho_p c_p (T_s - T_0) \quad (3)$$

where λ is thermal conductivity, ρ is density, c is heat capacity; subscript s refers to surface values; subscript p refers to propellant and g refers to gas. The quantity Q_s is the energy release in the surface zone that is to be computed. The physical parameter values used are: $\lambda_g = 1.2 \times 10^{-4}$ cal/cm-sec-°K, $\rho_p = 1.54$ g/cm³, $c_p = 0.35$ cal/g-°K. The results of the computations are shown in Fig. 10. Again the scatter is rather high but now no clear difference between the catalyzed and noncatalyzed propellants emerges. Both values are comparable at comparable burning rates (Q_s is not a pressure-related function but rather temperature-related, thus burning rate, not pressure, is the abscissa). Both values increase comparably with burning rate reflecting, presumably, the increasing surface temperature. Thus, despite the indicated alteration in the chemical pathway deduced from Fig. 6, the surface energetics are evidently not greatly altered by catalysis.

We have shown that the dark zone and flame zone reactions have little influence on the burning rate. However, an understanding of the dark zone and flame zone reaction is necessary for the prediction of flow processes in rocket motors in which the dark zone reaction time is an appreciable fraction of the residence time of the chamber gases. In such motors, the gas temperature at the throat is significantly lower than the fully reacted temperature and, as a result, the mass discharge rate through the throat is higher than anticipated. This can lead to the type of instabilities described in Ref. 17 which used the dark zone results of Fig. 4 in the prediction of transient motor performance.

Summary and Conclusions

Studies of the zones in the combustion wave of catalyzed nitrate ester propellants show that each zone is altered somewhat by the rate-accelerating metal salts. However, the alteration that is directly responsible for the increase in burning rate is enhancement of the net rate of reaction in the fizz zone. The consequent increase in conductive feedback to the burning surface increases its temperature and, thereby, boosting its degradation/gasification rate, hence, the burning rate. Conceivably, this increase in fizz zone feedback could have been augmented (or opposed) by changes in the surface energetics. Changes in the surface chemistry are apparent but accompanying changes in the energetics are not found.

The overall results reported here are not fully consistent with the models of Camp or Powling, et al. The simultaneous changes in surface chemistry and fizz zone reaction rate suggest a model that relates the two causally. A model which shows quantitatively how the super rate can arise and then disappear to yield a plateau is developed in Ref. 18.

List of Abbreviations

Propellant Ingredients	
NC	- Nitrocellulose
NG	- Nitroglycerine
PNC	- Particulate nitrocellulose (Naval Ordnance Station at Indian Head).
TMETN	- Trimethylolethane trinitrate (Trojan Powder Co.).
EC	- N,N' - Diethylcarbanilide (Eastman Organic Chemicals).
Additives	
PbSa	- Normal lead salicylate (National Lead Co.).
Pb2-EH	- Lead 2-ethylhexoate (National Lead Co.).
CuSa	- Monobasic cupric salicylate (National Lead Co.).
C	- Carbon Powder (Columbian Carbon Co. Neo Spectra TA).

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Acknowledgments

The authors are indebted to A. T. Camp and C. E. Johnson of the Naval Propellant Plant at Indian Head, Maryland, for advice on the manufacture of the PNC/MTN propellants.

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Table I

Specifications of all PNC/TMETN propellant formulations used for this study.

BATCH NO.*	BASIC COMPOSITION %				ADDITIVES %			COMMENT
	PNC	TMETN	TEGDN	EC**	C	PbSa	CuSa	
1026, 1055, 1029, 1056, 1031, 1038, 1039, 1044, 1045	53.70	39.10	7.02	0.08	0.10			
	52.65	38.33	6.88	0.08	0.10	0.98	0.98	L
	52.65	38.33	6.88	0.08	0.10	0.98	0.98	S
	53.76	39.13	7.03	0.08				
	50.00	40.40	7.02		PbSa 1.20	Pb2EH 1.20		H
	53.29	38.70	6.85	0.08	0.10		0.98	S
	53.29	38.70	6.85	0.03	0.10	0.98		S

NOTE: L denotes unground additives (PbSa ~ 10 μ and CuSa ~ 10 μ).
S denotes ground additives (PbSa ~ 3 μ and CuSa ~ 3 μ).
H denotes additives mixed with heptane.
Nitrogen in PNC is 12.6%.

*Propellants manufactured at the Guggenheim Laboratories of Princeton University.

**Because PNC, TMETN, and TEGDN contain EC the total EC in the propellant is 1.7%.

Table II

Overall reaction order n in dark zone determined from burning rate index m and dark zone index d .

PROPELLANT TYPE	CATALYST	PRESSURE RANGE, ATM	m	d	n	REFERENCE
PNC/TMETN NO. 1026	NO CATALYST	15 - 60	0.80	-1.69	2.49	THIS STUDY
PNC/TMETN NO. 1029	1% CuSa 1% PbSa	15 - 60	0.45	-1.96	2.41	THIS STUDY
PNC/TMETN NO. 1031	1% CuSa 1% PbSa	15 - 60	0.28	-2.27	2.55	THIS STUDY
NC/NG	NO CATALYST	20 - 100	0.56	-1.95	2.51	HEATH REF. 10
NC/NG	NO CATALYST	11 - 35	0.60	-2.20	2.80	HELLER REF. 12
NC/NG	NO CATALYST	17 - 41	0.45	-2.00	2.45	CRAWFORD REF. 8,9

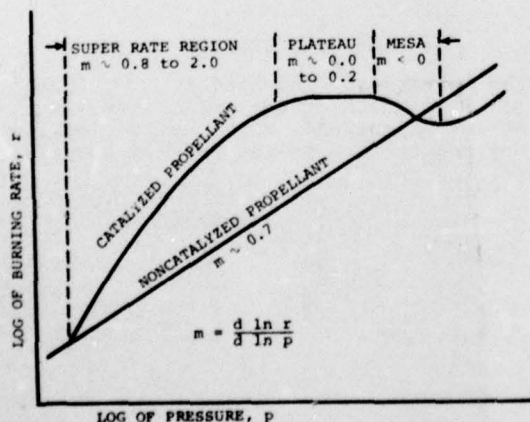


Fig. 1 Definition of super rate, plateau and mesa-burning.

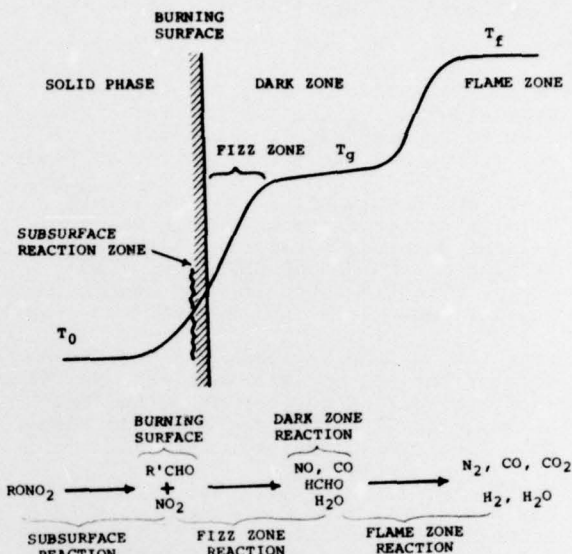


Fig. 2 Combustion zones and processes of double base propellant.

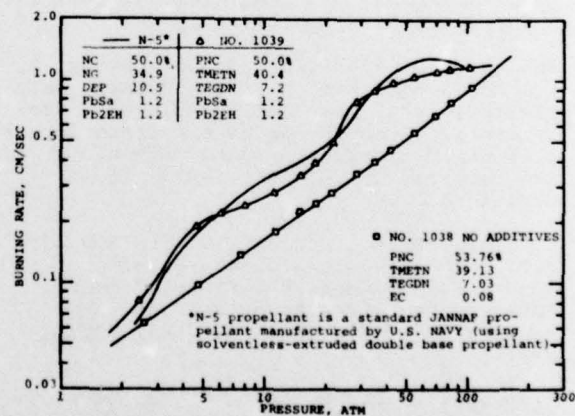


Fig. 3 Comparison of plateau burning rate of NC/NG and PNC/TMETN propellants showing that the super rate characteristics are comparable when TMETN replaces NG.

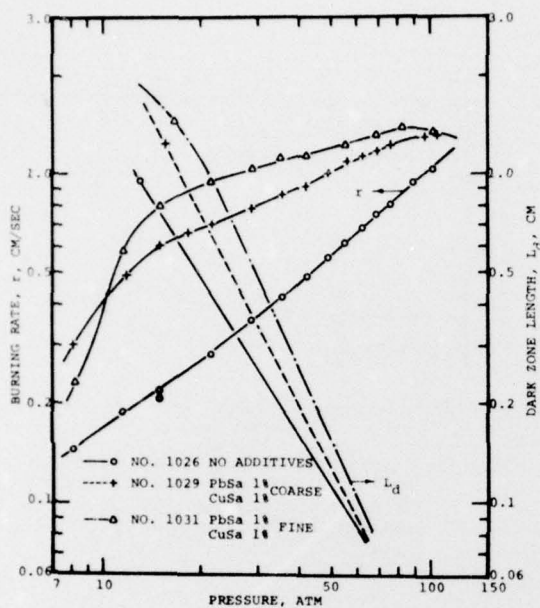


Fig. 4 Effect of burning rate on dark zone length showing lengthening of dark zone with higher burning rates.

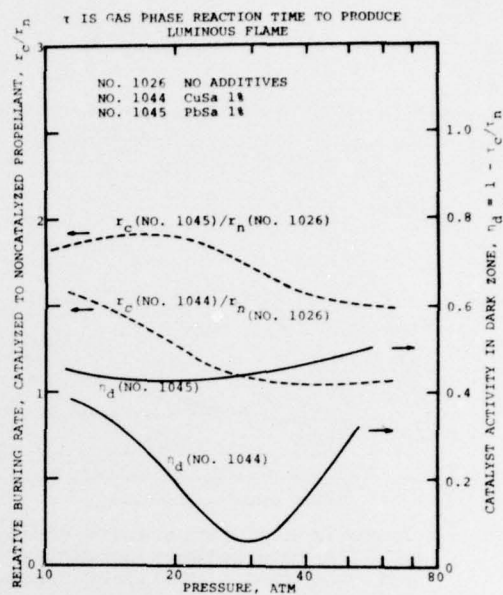


Fig. 5b Catalyst activity in dark zone and relative increase in burning rate as functions of pressure; the parameter is catalyst type.

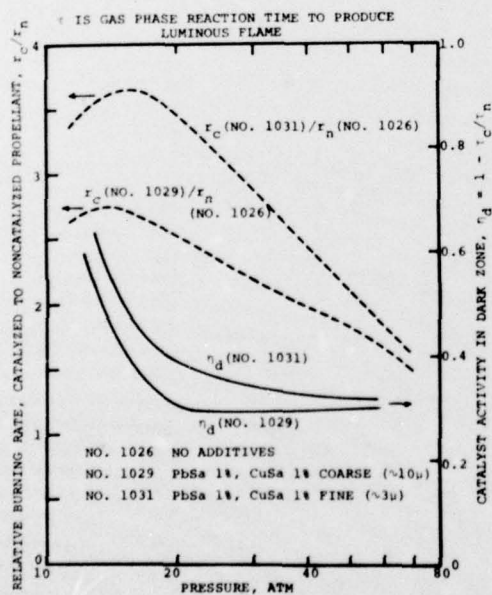


Fig. 5a Catalyst activity in dark zone and relative increase in burning rate as functions of pressure; the parameter is catalyst particle size. (Larger values of η_d imply accelerated reaction in the dark zone.)

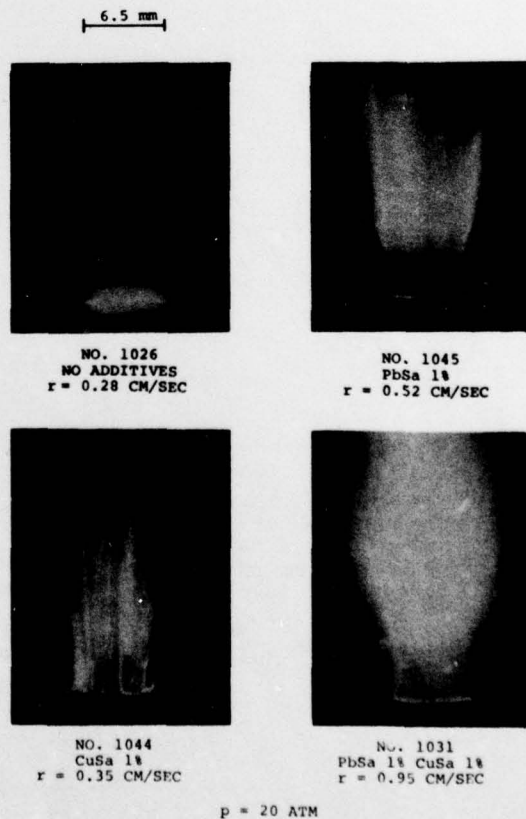


Fig. 6 Effect of catalyst on flame structure showing ejected particles from burning surface of catalyzed propellant (photographed using IR film).

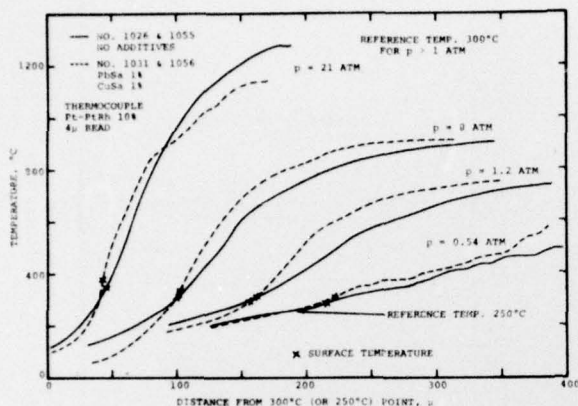


Fig. 7 Comparison of temperature profiles in fizz zone between noncatalyzed and catalyzed propellants, showing that catalysts accelerate fizz zone reactions.

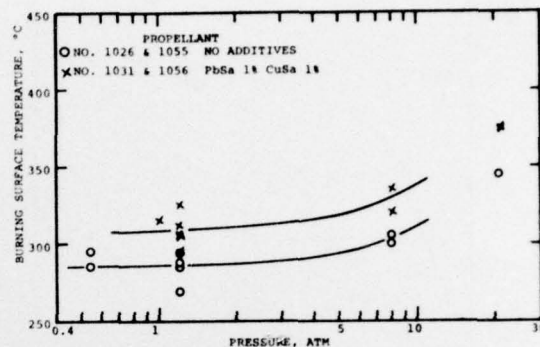


Fig. 9 Dependence of burning surface temperature on pressure and comparison of burning surface temperature of catalyzed and noncatalyzed propellant.

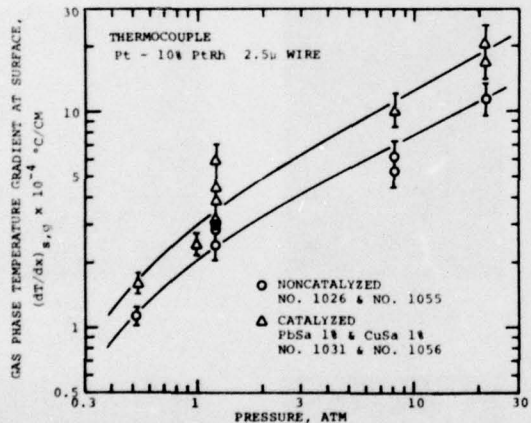


Fig. 8 Gas phase temperature gradient at the burning surface showing higher rate of heat feedback from gas phase to condensed phase when propellant is catalyzed.

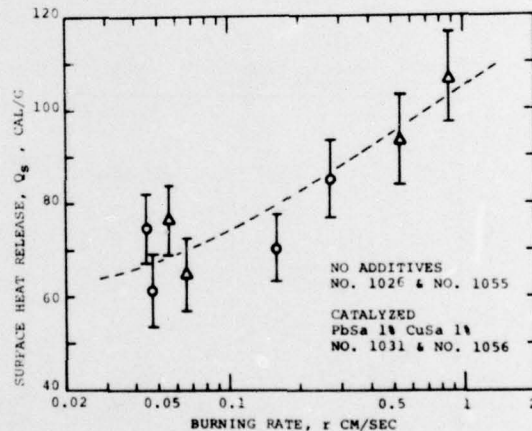


Fig. 10 Relationship between the surface heat release and the burning rate showing no detectable difference in Q_s between noncatalyzed and catalyzed propellants.